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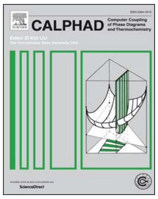

Reconciling SGTE and ab initio enthalpies of the elements

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ABSTRACT

The CALPHAD framework is built on assumption that all phases have a well-defined free energy over all accessible composition, temperature and pressure conditions. Unfortunately, it is common for phases to exhibit mechanical instabilities in at least some range of conditions, thus precluding direct experimental measurements and hindering computational efforts. A pragmatic solution has often been to extrapolate free energies from stable region into the unstable regions, but extrapolations from different systems that share a common phase may not agree and extrapolated free energies can unintentionally lie below the free energy of stable phases. Computational approaches that aim to directly calculate the free energy of unstable phases offer a promising avenue to address these issues. Among them, the recently proposed "inflection detection" scheme lies on a strong theoretical footing. We provide further support for this approach by demonstrating that it yield free energies that agree very well with the widely used SGTE (Scientific Group Thermodata Europe) data for pure elements. This finding suggest that it may be possible to get the best of both worlds: obtain a theoretically justified definition of the free energy of mechanically unstable phases and preserve much of existing empirical standards for the assignments of such free energies.

1. Introduction

The CALPHAD formalism [1–6] fundamentally relies on the ability to assign a well-defined free energy to all phases over all accessible composition ranges and temperature-pressure conditions. Unfortunately, mechanical instabilities are common in solid-state systems [7–10], making it difficult to measure or even calculate suitable free energies. This problem has prompted a long search for reasonable and practical definitions of the free energies of mechanically unstable phases [1,8,11,9,12–14,10] and still hinders thermodynamic database development [13]. To address this issue, a simple computational scheme, called "inflection-detection", was recently proposed [15]. Although this scheme has already been shown to have a sound theoretical basis, its adoption will be more likely if it yields free energies for mechanically phases of the elements that are in agreement with the widely used SGTE (Scientific Group Thermodata Europe) values [16]. This paper investigates this important question and confirms that inflection-detection and SGTE enthalpy values indeed agree very well. This finding suggests that the inflection-detection concept does capture, in a formal framework, the essence of what CALPHAD practitioners have been doing more intuitively for decades.

Having a practical, systematic and formal way of assigning free energies to mechanically unstable phases solves many of the problems the CALPHAD community often encounters. The common practice of extrapolating the free energy of an unstable phase from the free energy in composition regions where the phase is stable is not without problems. Extrapolations from different directions in composition-temperature-pressure space may not agree and the extrapolated free energy of an unstable phase risk inadvertently lying below the free energy of a truly stable phase.

This paper is organized as follows. We first summarize the theoretical basis for the inflection-detection method before presenting an extensive comparison of the resulting ab initio and SGTE enthalpies. We then discuss the implications and the interpretation of these findings.

2. Theory

It has recently been proposed [15] that the point of lowest energy at the onset of mechanical instability provides a logically consistent definition of the energy of a mechanically unstable phase. For completeness and clarity, we summarize the main features of this approach below (refer to Fig. 1).

In a system of N atoms, let x denote the $3N$ vector of all atomic positions (and unit cell parameter, if the system is periodic), let $V(x)$ denote the potential energy of the system in that state and let $\varkappa(x)$ be the minimum curvature at x, that is, the minimum eigenvalue of the Hessian (the matrix of second derivatives). The set of coordinates x such that $\varkappa(x) > 0$ and $\varkappa(x) \leq 0$ correspond to mechanically stable and unstable regions, respectively. Given an ideal structure x^u in which atoms are not allowed to relax away from their ideal positions, we define its

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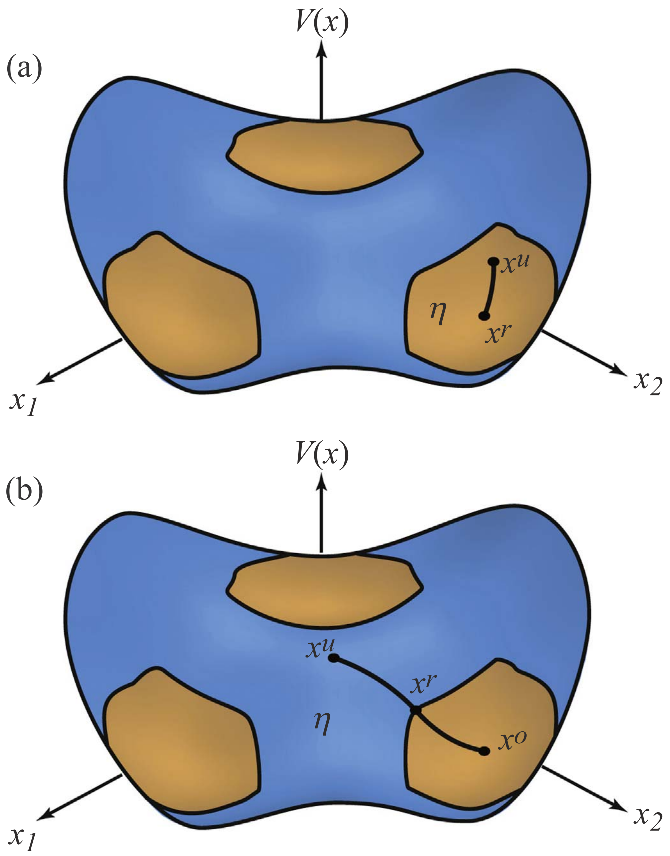

Fig. 1. Inflection-detection method. The potential energy hypersurface $V(x)$ (as a function of the state x of the system) defines a natural partitioning of phase space into neighborhoods η, based on the sign of $\varkappa(x)$, the local minimum curvature of $V(x)$ (blue: negative, yellow: positive). Each neighborhood (stable or not) can be assigned a well-defined energy by finding the minimum energy within that neighborhood. (a) In the case of a mechanically stable structure, the initial unrelaxed structure x^u simply relaxes to a local minimum x^r. (b) For a mechanically unstable structure, an unconstrained minimization would yield the over-relaxed point x^o which is actually the energy of another structure. The inflection detection method instead finds x^r, the minimum energy within η, which is located at an inflection point where the minimum curvature $\varkappa(x)$ changes sign. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

neighborhood η as the largest connected set containing x^u over which the minimum curvature $\varkappa(x)$ does not change sign. Now, we define the energy E associated with x^u as the minimum of the potential $V(x)$ over all x in the neighborhood η. When x^u is in a mechanically stable region, E is just the potential energy $V(x^r)$ at the lowest local interior minimum x^r in η, which agrees with the usual notion of energy of a relaxed structure. When x^u is in a mechanically unstable region, $E = V(x^r)$ as well, but now x^r must be at the boundary of η, i.e., a point where $\varkappa(x)$ is zero. Specifically, x^r is the point of minimum energy subject to the constraint that $\varkappa(x^r) = 0$. This method is called "inflection detection" because, for a mechanically unstable structure, if one relaxes the system from the unrelaxed position x^u, one will first detect an inflection point at x^r before finding the local minimum at x^o.

At finite temperature T, the relevant thermodynamic quantity is the free energy and the simple expression for the energy $E = V(x^r)$ must be replaced by a suitable integral over the whole neighborhood η [15]:

$$F_{vib} = -k_B T \ln\left(\int_{x\in\eta} \exp(-V(x)/(k_B T))dx\right) \quad (1)$$

where k_B is Boltzmann's constant. It can be verified that this expression converges to $V(x^r)$ as $T \to 0$. This free energy solely includes the contribution of lattice vibrations to the free energy. Configurational and electronic contributions can be added to it in the usual way [17]. In this work, configurational terms are absent because we focus on pure elements and electronic excitation terms are neglected, as they are typically small.

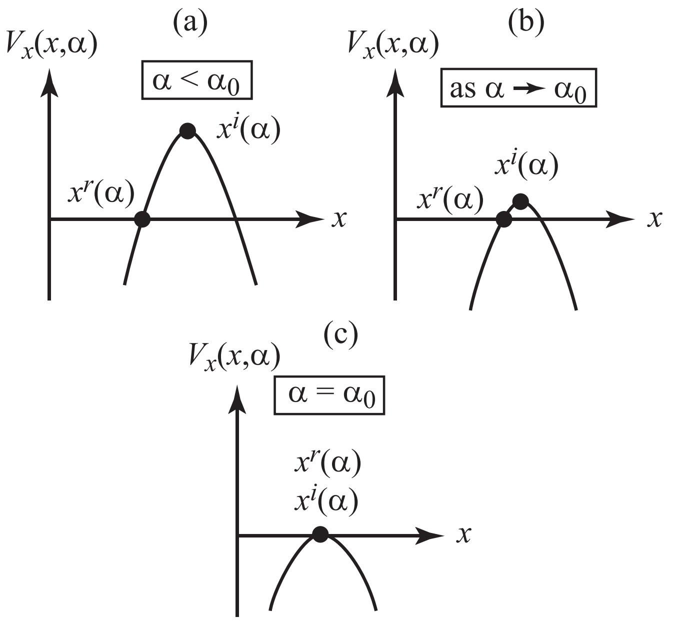

Fig. 2. Behavior of the potential energy in the vicinity of the onset of mechanical instability. The first derivative of the potential energy of the system $V_x(x, \alpha)$ as a function of the system's state x is represented, with panels (a), (b) and (c) showing the effect of varying the value of some external parameter α (such as composition or pressure). This illustrates that the disappearance of a local minimum $x^r(\alpha)$ (in panel (c)) must be accompanied by merging of an inflection point $x^i(\alpha)$, a local minimum $x^r(\alpha)$ at $\alpha = \alpha_0$.

This definition of the (free) energy offers three desirable properties [15]. First, it is based on the intuitive geometrical notion of curvature and, as a result, efficient numerical methods are readily available to identify either the local minimum or the inflection point [18].

Second, when a system approaches the onset of mechanical instability (e.g. as composition varies) the local minima disappears by merging with a nearby inflection point, for any physically reasonable potential surface. This is best understood in a one-dimensional example. Consider the potential $V(x, \alpha)$ for different values of some control variable α (which could be composition, for instance). Fig. 2 show the behavior of the derivative of this potential with respect to x, denoted $V_x(x, \alpha)$ as α varies. As α approaches the point of instability at some value α_0, the local minimum (where $V_x(x, \alpha) = 0$) must approach the maximum of $V_x(x, \alpha)$ (where the second derivative $V_{xx}(x, \alpha) = 0$). But $V_{xx}(x, \alpha) = 0$ is nothing but the potential's inflection point. Hence, the energy is a continuous function of composition, even across an instability and even if it tracks the minimum in the stable region $\alpha < \alpha_0$ and the inflection point in the unstable region $\alpha > \alpha_0$. At finite T, the transition is even smoother, thanks to the smoothing effect of the integration over η in Eq. (1).

Finally, the approach has a very convenient practical property. It is well-known that, for stable phases, one can usually accurately evaluate Eq. (1) in the harmonic approximation. Remarkably, using inflection-detection, this remains true for unstable phases, because the inflection point structure x^r is, by construction, only unstable along at most a small finite number of modes (the number of which is negligible in the thermodynamic limit of an infinite number of modes). Hence, one can use a harmonic expansion about x^r and simply ignore the unstable modes (since they occupy a infinitesimal fraction of the Brillouin zone).

3. Numerical experiment

The calculated energies were obtained with the VASP software [19,20] implementing the Projector-augmented wave method [21,22].